

## Electrical Resistivity of Cubanite: $\text{CuFe}_2\text{S}_3$

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The electrical resistivity of a single crystal of cubanite,  $\text{CuFe}_2\text{S}_3$ , has been determined from 4.2 to 340 K. Definite semiconducting behavior is observed, showing that the rapid electron exchange between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in  $\text{Cu}^{1+}\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_3$  is confined to the edge-shared pairs of iron-sulfur tetrahedra.

### Introduction

Cubanite,  $\text{CuFe}_2\text{S}_3$ , is a well known, weakly ferromagnetic mineral whose structure is related to wurtzite (1-3). However, copper and iron are ordered, and the symmetry is orthorhombic. Both copper and iron are tetrahedrally surrounded by sulfur, and the unusual feature of this structure is that the iron tetrahedra share edges in pairs. On heating to about 210°C cubanite "irreversibly" transforms to a cubic phase (4). Despite many attempts (4), cubanite has never been synthesized except by nature.

Two formal oxidation state situations can be proposed for cubanite:  $\text{Cu}^{2+}\text{Fe}_2^{2+}\text{S}_3$  or  $\text{Cu}^{1+}\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_3$ . Since all iron is on identical crystallographic sites, a  $\text{Cu}^{2+}\text{Fe}_2^{2+}\text{S}_3$  valence combination has some appeal. However, Mössbauer data (5, 6) indicate a  $\text{Cu}^{1+}\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_3$  situation with rapid electron exchange between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . Thus, it has been suggested (7) that cubanite is metallic. The purpose of this paper is to show that cubanite is not metallic and that nonmetallic properties can be consistent with the  $\text{Cu}^{1+}\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_3$  formulation.

### Experimental

Our sample of cubanite came from Falconbridge, Onaping, Ontario, Canada and was obtained through Minerals Unlimited. A bar for resistivity measurements was cut from this sample and shown to be a single crystal by X-ray precession photographs.

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An X-ray powder pattern of our cubanite sample was obtained with a Hägg-Guinier camera using  $\text{CuK}\alpha_1$  radiation and an internal standard of KCl ( $a = 6.2931 \text{ \AA}$  at 25°C). A least-squares refinement of the cell dimensions with this accurate data gave:  $a = 6.4683 \pm .0008 \text{ \AA}$ ,  $b = 11.121 \pm .001 \text{ \AA}$ , and  $c = 6.2314 \pm .0009 \text{ \AA}$ . This is in excellent agreement with other reported cell dimensions (2, 3) and suggests that cubanite is always very close to its ideal composition.

The magnetic moment of our cubanite sample was measured from 4.2 to 298 K. An essentially constant moment of about 1 emu/gm was observed over this temperature range. This agrees well with the magnetic data of Sawada, Ozima, and Fujiki (8).

### Results

The electrical resistivity of our crystal of cubanite was measured by the four probe method from 4.2 K to 340 K. The resistivity was  $10^8$  ohm-cm at 4.2 K and decreased with increasing temperature to a value of 17 ohm-cm at 340 K. The actual values of resistivity may not be very meaningful since a mineral sample is not expected to be sufficiently pure to show intrinsic electrical properties. Nonetheless, we can unambiguously conclude that cubanite is not metallic.

### Discussion

The valence distribution in  $\text{CuFeS}_2$  is definitely known to be  $\text{Cu}^{1+}\text{Fe}^{3+}\text{S}_2$ . The average Cu-S distances are 2.34 Å in both  $\text{CuFeS}_2$  and cubanite.

However, the average Fe-S distance is somewhat longer in cubanite than  $\text{CuFeS}_2$  (2.27 Å and 2.22 Å, respectively). This is then entirely consistent with a  $\text{Cu}^+\text{Fe}^{2+}\text{Fe}^{3+}\text{S}_3$  situation for cubanite since  $\text{Fe}^{2+}$  is expected to be larger than  $\text{Fe}^{3+}$ . Certainly these distances suggest that a  $\text{Cu}^{2+}\text{Fe}_2^{2+}\text{S}_3$  situation in cubanite is very unlikely. Furthermore, the Mössbauer data (5, 6) for cubanite show only one type of iron to be present with an isomer shift which is midway between the isomer shifts expected for  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in tetrahedral coordination. This indicates that there is rapid electron exchange between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  such as occurs in  $\text{Fe}_3\text{O}_4$ .

Cubanite can thus be viewed as  $\text{Cu}^+\text{Fe}_2^{3+}\text{S}_3$  plus an electron which rapidly moves between iron atoms. If the electron is free to move from any iron to any other iron, metallic behavior would be expected. However, if the rapid electron exchange is confined to the Fe-Fe pairs, then metallic properties would not be expected. Our electrical measurements show that the rapid electron exchange in cubanite is restricted to the "clusters" of edge-shared iron tetrahedra.

Since the mobile electron belongs equally to both irons of the cluster, its spin should be antiparallel to the other five electrons on each of the irons of the cluster. The two irons of the cluster would be ferromagnetically coupled to each

other, and the net moment of the cluster would be  $9 \mu_B$ . Mössbauer data (5, 6) clearly show that cubanite is magnetically ordered at room temperature and below, but the magnetic moment of cubanite is too low for any simple ferromagnetic or ferrimagnetic model. Thus, it appears that the ferromagnetic clusters order in a basically antiferromagnetic arrangement with respect to each other and that the observed magnetic properties are best described as parasitic ferromagnetism.

#### Acknowledgment

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